

We claim:

1. A process for preparing solid polymeric pressure sensitive adhesive microspheres comprising:

- (a) contacting a polymerizable aqueous emulsion of at least one non-ionic monomer of an alkyl acrylate or alkyl methacrylate ester of a non-tertiary alcohol and at least one ionic monomer copolymerizable with said non-ionic monomer and at least one non-free radically polymerizable acid; and
- (b) polymerizing the emulsion to form an aqueous suspension of said solid polymeric pressure sensitive adhesive microspheres;

wherein said non-free radically polymerizable acid is contacted with said polymerizable aqueous emulsion prior to achieving about 95% conversion of said non-ionic monomer.

2. The process of claim 1 wherein the alkyl group of said non-ionic monomer has from 4 to about 14 carbon atoms.

3. The process of claim 2 wherein said non-ionic monomer is selected from 2-ethyl hexyl acrylate or n-butyl acrylate.

4. The process of claim 1 wherein said ionic monomer is an alkali metal, ammonium or amine salt of an acid selected from a monoolefinic monocarboxylic acid, a monoolefinic dicarboxylic acid or mixtures thereof.

5. The process of claim 4 wherein said ionic monomer is an alkali metal, ammonium or amine salt of acrylic acid.

6. The process of claim 5 wherein said ionic monomer is ammonium acrylate or sodium acrylate.

7. The process of claim 4 wherein said ionic monomer is produced *in situ* by reaction of an acid selected from a monoolefinic monocarboxylic acid, a

monoolefinic dicarboxylic acid or mixtures thereof with a compound selected from an alkali metal hydroxide, ammonium hydroxide or an amine, and wherein said non-free radically polymerizable acid is contacted with said polymerizable aqueous emulsion after formation of said ionic monomer.

8. The process of claim 1 wherein said non-free radically polymerizable acid is selected from acetic acid, hexanoic acid, phenyl undecanoic acid, stearic acid, hydrochloric acid, sulfuric acid or mixtures thereof.

9. The process of claim 8 wherein said non-free radically polymerizable acid is sulfuric acid.

10. The process of claim 1 wherein an oil soluble, low water soluble initiator is added to said polymerizable aqueous emulsion and polymerization initiated after said non-free radically polymerizable acid is contacted with said polymerizable aqueous emulsion.

11. The process of claim 1 wherein an oil soluble, low water soluble initiator is added to said polymerizable aqueous emulsion and polymerization initiated before said non-free radically polymerizable acid is contacted with said polymerizable aqueous emulsion.

12. The process of claim 1 further comprising adding a water soluble initiator to the polymerization mixture after achieving about 90% conversion of said non-ionic monomer.

13. The solid polymeric pressure sensitive adhesive microspheres produced by the process of any of claims 1,2,3,4,5,6,7,8,9,10,11 or 12.

14. A process for preparing solid polymeric pressure sensitive adhesive microspheres comprising:

(a) forming a polymerizable aqueous emulsion by contacting water, at least one non-ionic monomer of an alkyl acrylate or alkyl methacrylate ester of a non-tertiary alcohol, at least one ionic monomer

copolymerizable with said non-ionic monomer, and at least one emulsifier;

(b) initiating polymerization;

(c) adding at least one non-free radically
5 polymerizable acid; and

(d) polymerizing the non-free radically
polymerizable acid-containing mixture to form the solid
polymeric pressure sensitive adhesive microspheres;

wherein said non-free radically polymerizable acid is
10 added to said polymerizable aqueous emulsion prior to
achieving about 95% conversion of said non-ionic monomer.

15. The process of claim 14 wherein the alkyl group
of said non-ionic monomer has from 4 to about 14 carbon
atoms.

15 16. The process of claim 15 wherein said non-ionic
monomer is selected from 2-ethyl hexyl acrylate or n-butyl
acrylate.

17. The process of claim 14 wherein said ionic
monomer is an alkali metal, ammonium or amine salt of an
20 acid selected from a monoolefinic monocarboxylic acid, a
monoolefinic dicarboxylic acid or mixtures thereof.

18. The process of claim 17 wherein said ionic
monomer is an alkali metal, ammonium or amine salt of
acrylic acid.

25 19. The process of claim 18 wherein said ionic
monomer is ammonium acrylate or sodium acrylate.

20. The process of claim 17 wherein said ionic
monomer is produced *in situ* by reaction of an acid
selected from a monoolefinic monocarboxylic acid, a
30 monoolefinic dicarboxylic acid or mixtures thereof with a
compound selected from an alkali metal hydroxide, ammonium
hydroxide or an amine.

21. The process of claim 14 wherein said non-free
radically polymerizable acid is selected from acetic acid,

hexanoic acid, phenyl undecanoic acid, stearic acid, hydrochloric acid, sulfuric acid or mixtures thereof.

22. The process of claim 21 wherein said non-free radically polymerizable acid is sulfuric acid.

5 23. The process of claim 14 wherein step (b) is conducted in the presence of an oil soluble, low water soluble initiator.

24. The process of claim 14 further comprising adding a water soluble initiator to the polymerization mixture
10 after achieving about 90% conversion of said non-ionic monomer.

25. Solid acrylic pressure sensitive adhesive microspheres produced by the process of any of claims 14,15,16,17,18,19,20,21,22,23 or 24.

15 26. A process for preparing solid polymeric pressure sensitive adhesive microspheres comprising:

(a) contacting a polymerizable aqueous emulsion of 2-ethyl hexyl acrylate and an alkali metal, ammonium or amine salt of acrylic acid, and sulfuric acid;

20 and

(b) polymerizing the emulsion to form an aqueous suspension of said solid polymeric pressure sensitive adhesive microspheres;

wherein said sulfuric acid is contacted with said
25 polymerizable aqueous emulsion prior to achieving about 95% conversion of said 2-ethyl hexyl acrylate.

27. The process of claim 26 further comprising adding a water soluble initiator to the polymerization mixture after achieving about 95% conversion of said non-
30 ionic monomer.